

Supporting Information

**A New View of Electrochemistry at Highly Oriented
Pyrolytic Graphite (HOPG)**

Anisha N. Patel, Manon Guille Collignon,⁺ Michael A. O'Connell, Wendy O. Y. Hung, Kim

M^cKelvey, Julie V. Macpherson and Patrick R. Unwin*

Department of Chemistry, University of Warwick, Coventry, CV4 7AL, UK

*Corresponding author: P.R.Unwin@Warwick.ac.uk

⁺ Present address: Laboratoire PASTEUR, Ecole Normale Supérieure, CNRS, UPMC
Univ Paris 06, Département de Chimie, 24 Rue Lhomond, Paris, France.

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S.1 Capacitance measurements. Capacitance values were extracted from simple CV measurements in 1 M KCl at 0.1 V s⁻¹. Figure S1 shows data for three types of HOPG: (a) SPI-1, (b) ZYA and (c) AM, where freshly exposed surfaces for the first two were produced by cleaving with scotch tape and the latter by mechanical cleavage. Each cycle shown is the initial CV for a freshly cleaved surface, which – in every case - was representative of subsequent cycles (up to 10 runs), within $\pm 2\%$. The capacitance was extracted as the current amplitude at 0.05 V. For SPI-1 grade the capacitance was $2.9 \pm 1.2 \mu\text{F cm}^{-2}$ (range 2.0 - 3.8 $\mu\text{F cm}^{-2}$). For ZYA grade, consistent values were obtained of $2.0 \pm 0.3 \mu\text{F cm}^{-2}$ (range 1.7 – 2.8 $\mu\text{F cm}^{-2}$). The lowest values are consistent with the best reported in the early literature where very slow kinetics for $\text{Fe}(\text{CN})_6^{4-/3-}$ was proposed.^{S1} For AM samples the values obtained were $2.4 \pm 1.5 \mu\text{F cm}^{-2}$, however a histogram of the values obtained, Figure S1 (d), clearly shows that the majority of the values cluster between 0.7 $\mu\text{F cm}^{-2}$ and 2.2 $\mu\text{F cm}^{-2}$ with a few significant outliers which skews the overall data. Note that the lower values of 0.7 $\mu\text{F cm}^{-2}$ and 1.1 $\mu\text{F cm}^{-2}$ are close to the lowest observed value for this grade of HOPG cleaved mechanically.^{S2}

For HOPG (AM), cleaved mechanically, CVs of 1 mM $\text{Fe}(\text{CN})_6^{4-/3-}$ in 1 M KCl at 0.1 V s⁻¹ were run after measuring capacitance by quickly replacing the KCl solution with the redox mediator, in order to explore any possible correlations between capacitance and ET kinetics. A plot of the capacitance vs. ΔE_p for $\text{Fe}(\text{CN})_6^{4-/3-}$ redox is shown in Figure S2. For 10 different measurements carried out on freshly prepared surfaces, ΔE_p is essentially independent of capacitance. We ran 10 further measurements on freshly cleaved AM HOPG, without first measuring the capacitance. Statistically, a significant fraction of these surfaces would reasonably be expected to be of very high quality, and we again found ΔE_p in the range 59 to 69 mV.

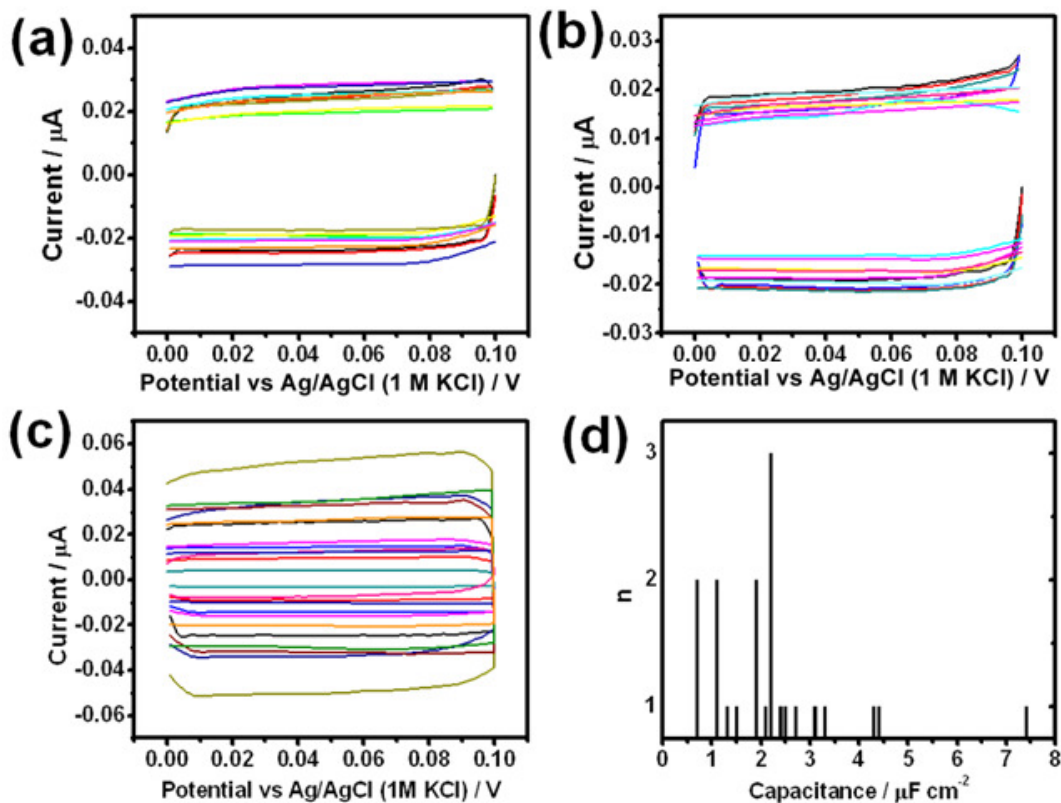


Figure S1. CVs showing the background currents for 1 M KCl at 0.1 V s⁻¹. Each cycle was run on freshly cleaved HOPG: (a) SPI-1, (b) ZYA and (c) AM, using the Teflon cell arrangement. (d) A histogram of capacitance values extracted from (c).

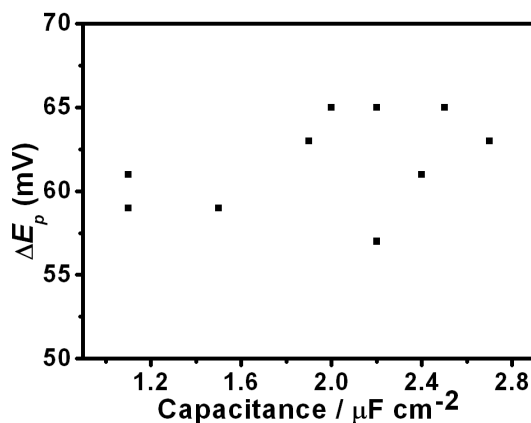


Figure S2. (a) Capacitance vs. ΔE_p for 1 mM ferrocyanide oxidation in 0.1 M KCl at 0.1 V s⁻¹ on the same surfaces.

S.2 Additional experimental details

(a) *Cells.* For all experiments carried out in the droplet arrangement, the cell was humidified in order to minimize solution evaporation, as described elsewhere.^{S3} The electrically-connected HOPG was placed on a small Perspex block which, in turn, sat on a

larger Teflon base, as shown in Figure S3 (ai). A larger glass cell body containing a small outlet hole was pushed over the Teflon base to create a tight seal. The cell was filled with water to a level slightly lower than the height of the Perspex block and deaerated with nitrogen or argon for 15 minutes. The freshly cleaved HOPG sample was then placed in the cell and a droplet of the solution of interest (either 10 μ l, with a diameter of \sim 3 mm, or 20 μ l, with a diameter \sim 5 mm) was gently placed on the surface of the HOPG in an area that by eye, appeared to be the most “shiny” and hence comprised the highest degree of the pristine basal surface as confirmed by FE-SEM and AFM. The droplet was typically placed on the HOPG surface within 1 min of sample cleaving, and the reference electrode and auxiliary electrode added. The cell was sealed using parafilm, and humidified by gently passing nitrogen gas through the droplet cell.

The Teflon cell arrangement utilized a cell with outer cylindrical dimensions of 8 mm diameter by 6 mm height, machined internally to a cylindrical diameter of 6 mm (4 mm in height), which decreased to a diameter of 3 mm (2 mm in height at the part closest to the substrate), as shown in Figure S3(aii). The bottom of the cell *was very* lightly greased with Apeizon wax, with any excess removed with tissue, and then positioned gently on the HOPG surface. The cell was filled with ca. 100 μ l of solution into which the auxiliary and reference electrodes were placed. Using this arrangement the electrode contact area was defined as a 3 mm diameter disc and it was possible to deaerate solution directly in contact with the HOPG surface (using nitrogen). However, we obtained similar results with and without deaeration of the solution and, consequently, most experiments were conducted without deaeration of the solution.

(b) Cleavage of HOPG. The following two methods were found to provide reproducible freshly exposed surfaces, on the commercially available grades of HOPG: ZYA, ZYH, SPI-1 and SPI-2, as verified by AFM (main text) and FE-SEM (SI section S5), and

complementary capacitance measurements (main text and section S1). For both procedures the PCB or silicon wafer-mounted HOPG was first secured onto a borosilicate glass slide, using double-sided adhesive tape. In the first method, single-sided Scotch tape was gently pressed onto the HOPG surface and then pulled off to remove the top layers, as shown in Figure S3(b). Alternatively, a second glass slide bearing double-sided adhesive tape was gently contacted to the HOPG basal surface and pulled vertically away from the substrate to reveal a freshly created surface (Figure S3(c)). We found that both cleaving methods produced similar surface topography and indistinguishable voltammetric responses. Consequently, the former was used mainly, since this procedure removed less HOPG layers for each cleave, enabling more experiments with each HOPG sample.

All HOPG (AM) samples were cleaved using a razor blade, as directed by Professor Richard McCreery in private correspondence. A fresh razor blade was gently inserted perpendicular to the basal plane and by gentle rocking of the blade through the sample, spontaneous cleavage of a piece of HOPG was encouraged. This cleaving method yielded HOPG pieces for which the cleaved area varied; only samples at least 1 x 1 cm. Initial capacitance measurements and voltammetric experiments were carried out with a droplet before using the Teflon cell. Both approaches yielded indistinguishable behavior.

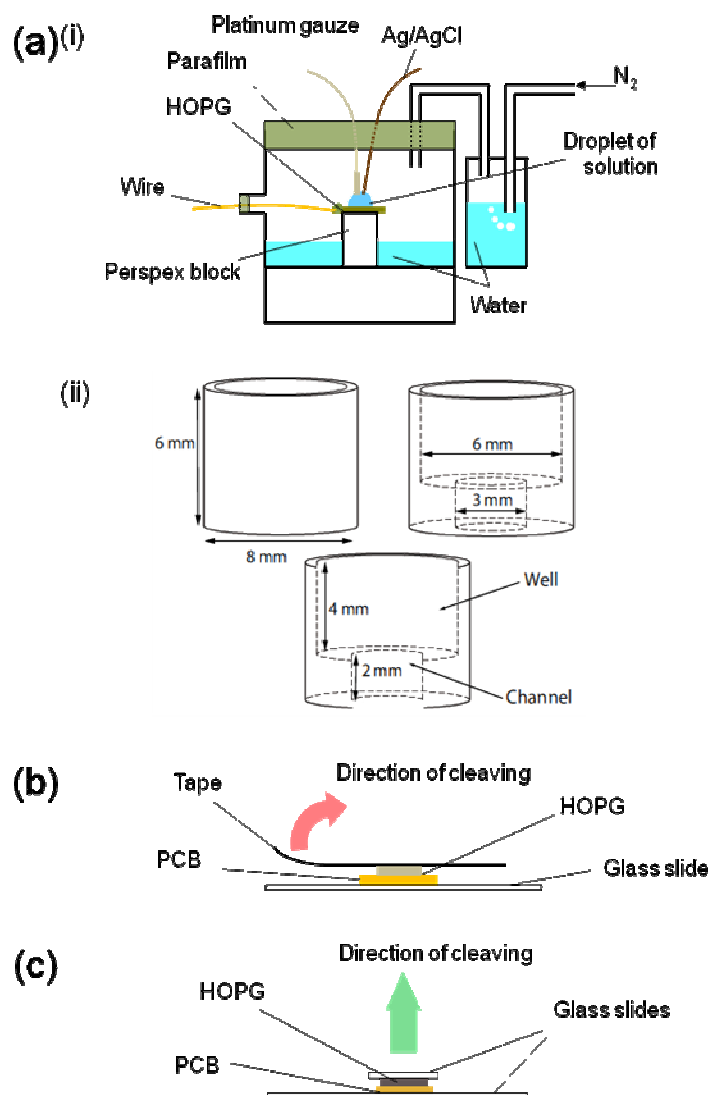


Figure S3. (a) (i) Schematic of the humidity cell used for some CV measurements on HOPG. Not to scale. (ii) Schematic of the Teflon cell used to hold solution on HOPG with a defined contact area. (b,c) Schematic of the two methods used to cleave commercial samples of HOPG.

S.3 CV behavior of $Fe(CN)_6^{4-/3-}$ in buffer solution. For comparison with data in the main paper, CVs were recorded in 0.1 M aqueous phosphate buffer (pH 7.2) at 0.1 V s^{-1} with SPI-1 grade HOPG using the Teflon cell arrangement, with each cycle run at 5 minute intervals. Figure S4 shows data for 1 mM $Fe(CN)_6^{4-}$ on initially freshly cleaved HOPG. The data show that the voltammetric waveshape changes with time, as found for non-buffered solutions reported in the main paper.

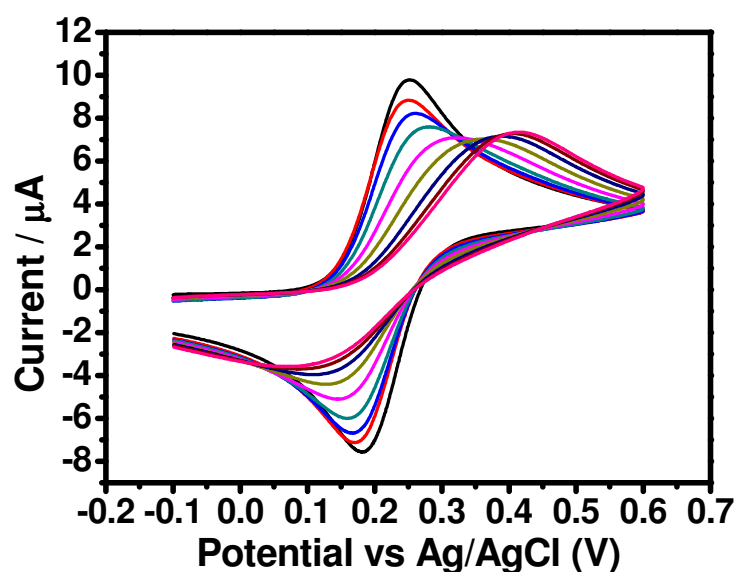


Figure S4. CVs showing repetitive cycles for the oxidation of 1 mM Fe(CN)_6^{4-} on SPI-1 grade HOPG in 0.1 M aqueous phosphate buffer (pH 7.2), run at 0.1 V s^{-1} .

S.4 Step edge analysis on basal plane HOPG by AFM. From AFM analysis of 69 images taken on ZYA, SPI-1, SPI-2, ZYH grade HOPG (scotch tape cleaved), and HOPG (AM) (mechanically cleaved), the step heights in terms of the number of graphite layers was calculated, producing the histograms shown in Figure S5 and summarized in Table 1 in the main paper. Figure S5 shows that ZYA, SPI-1 AM grades exhibit predominantly monolayer and bilayer steps, with AM, followed closely by ZYA grade, providing the optimum surface on which the density of step edges is minimized (Table 1, main text).

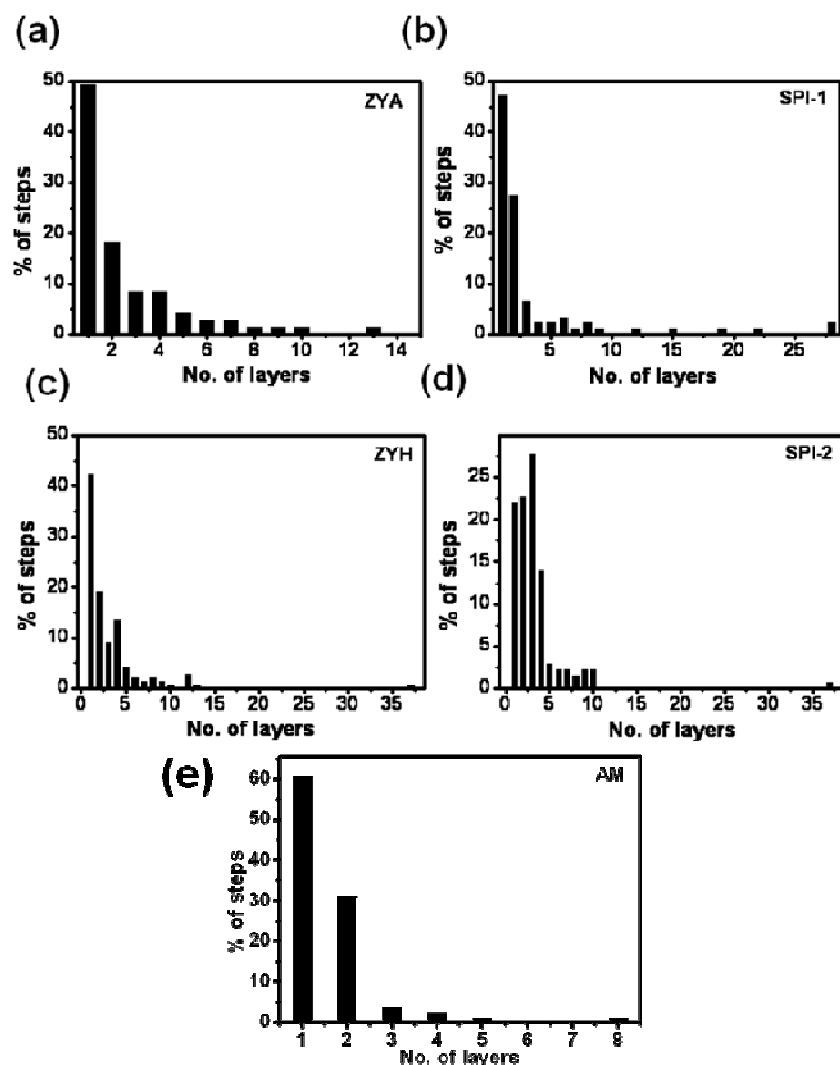


Figure S5. Histograms of step edge heights on different grades of freshly cleaved HOPG: (a) ZYA, (b) SPI-1, (c) ZYH, (d) SPI-2 grades and (e) AM.

S.5 Visualization of step edge density on HOPG by FE-SEM. To aid step edge visualization, Ag was electrodeposited from a solution containing 1 mM AgNO_3 in 1 M KNO_3 . A 3-electrode arrangement was employed and electrodeposition was promoted by closing the circuit at a potential of -0.4 V vs chloridized silver wire for 0.5 s. Figure S6 shows representative images of: (a) SPI-1 grade HOPG and (b) ZYA grade HOPG after electrodeposition, from which it can be seen that the density of step edges is clearly much lower on ZYA grade HOPG than for SPI-1, consistent with the AFM data reported in Figure 1 and Table 1 (main text). However, it can also be seen that both surfaces exhibit some

spatial heterogeneity in step separation. The average separation between two step edges ranges from approximately ~ hundreds of nm for SPI-1 grade to a few micrometers for ZYA grade, the latter in agreement with metal electrodeposition measurements on HOPG (AM) and ZYA grade HOPG samples.^{S4}

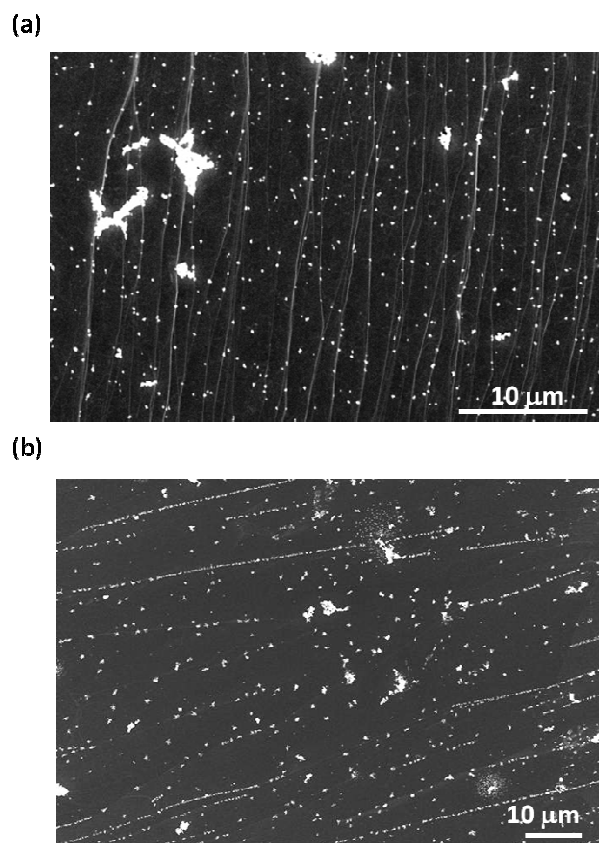


Figure S6. FE-SEM images of initially freshly cleaved HOPG: (a) SPI-1 and (b) ZYA, after Ag electrodeposition.

S.6 Time-dependent effects. Time-dependent studies carried out on $\text{Fe}(\text{CN})_6^{4-/3-}$ (main text Figure 3) were also carried out with $\text{Ru}(\text{NH}_3)_6^{3+}$. Figure S7 shows representative data for the reduction of 1 mM $\text{Ru}(\text{NH}_3)_6^{3+}$ in 0.5 M KCl at freshly cleaved HOPG (SPI-1 grade), using the Teflon cell (0.1 V s^{-1}) as a function of time, recorded every 5 minutes in the same solution for up to two hours. In this case there is very little variation in the ΔE_p , which ranged between ~64 mV (first scan) to 77 mV (last scan).

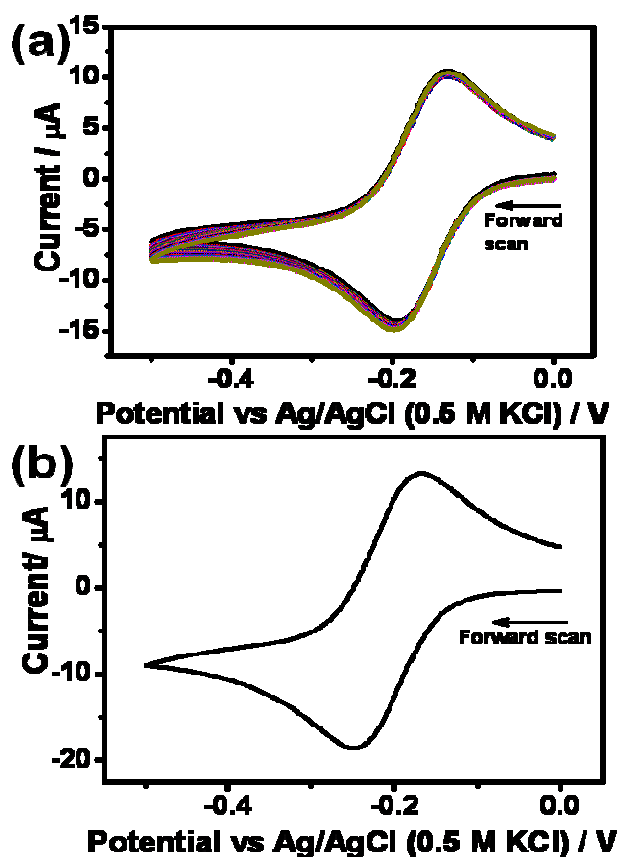


Figure S7. (a) Repeat CVs for the reduction of 1 mM $\text{Ru}(\text{NH}_3)_6^{3+}$ in 0.5 M KCl, at 0.1 V s^{-1} , on HOPG (SPI-1) with each CV run at 5 min intervals (total of 20 cycles). (b) CV for the reduction of 1 mM $\text{Ru}(\text{NH}_3)_6^{3+}$ in 0.5 M KCl, at 0.1 V s^{-1} , run on a surface that had first been subjected to 20 cycles of 1 mM $\text{Fe}(\text{CN})_6^{4-}$ in 1 M KCl, at 5 minute intervals on HOPG (SPI-1).

S.7 Additional C-AFM data

Figure S8 shows topography (i) and simultaneous C-AFM (ii) images for SPI-1 grade HOPG recorded immediately after cleaving (a) and 2 hours later (b). It can be seen that there is a significant decrease in conductivity over the surface, and that the changes are heterogeneous, as reported for more extensive times in the main text.

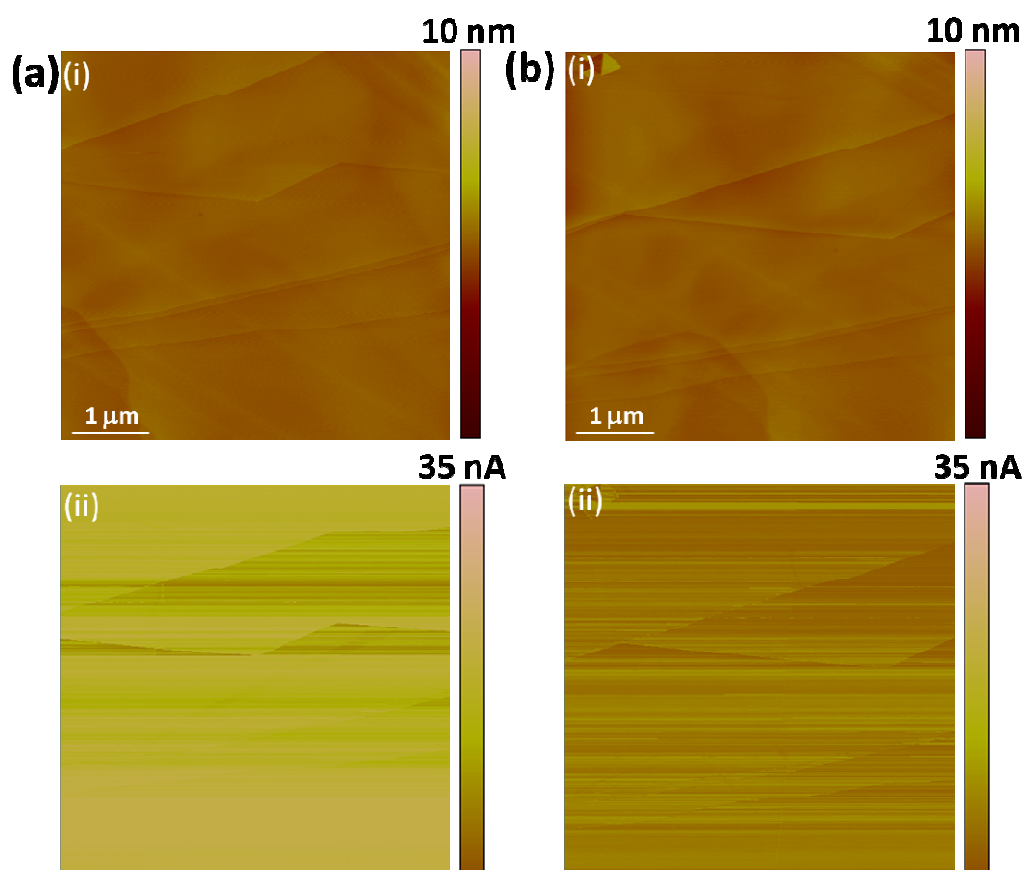


Figure S8. Topography (i) and simultaneous C-AFM (ii) images for SPI-1 grade HOPG recorded immediately after cleaving (a) and 2 hours later (b).

References

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